Chemical vapor deposition of WN$_x$C$_y$ using the tungsten piperidylhydrazido complex Cl$_4$(CH$_3$CN)W(N-pip): Deposition, characterization, and diffusion barrier evaluation

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(Received 7 October 2008; accepted 2 March 2009; published 30 June 2009)

The tungsten piperidylhydrazido complex Cl$_4$(CH$_3$CN)W(N-pip) (I) was used for film growth of tungsten carbonitride (WN$_x$C$_y$) by metal-organic chemical vapor deposition (CVD) in the absence and presence of ammonia (NH$_3$) in H$_2$ carrier. The microstructure of films deposited with NH$_3$ was x-ray amorphous between 300 and 450 °C. The chemical composition of films deposited with NH$_3$ exhibited increased N levels and decreased C levels over the entire deposition temperature range (300–700 °C) as compared to films deposited without NH$_3$. As determined by x-ray photoelectron spectroscopy, W is primarily bonded to N and C for films deposited at 400 °C, but at lower deposition temperature the binding energy of the W–O bond becomes more evident. The growth rates of films deposited with NH$_3$ varied from 0.6 Å/min at 300 °C to 4.2 Å/min at 600 °C. Over 600 °C, the growth rate decreased when using NH$_3$ presumably due to parasitic gas phase reactions that deplete the precursor. Diffusion barrier properties were investigated using Cu/WN$_x$C$_y$/Si stacks consisting of 100 nm Cu deposited at room temperature by reactive sputtering on a 20 nm WN$_x$C$_y$ film deposited at 400 °C by CVD. X-ray diffraction and cross-sectional transmission electron microscopy were used to determine the performance of the diffusion barrier. Cu/WN$_x$C$_y$/Si stacks annealed under N$_2$ at 500 °C for 30 min maintained the integrity of both Cu/WN$_x$C$_y$ and WN$_x$C$_y$/Si interfaces. © 2009 American Vacuum Society. [DOI: 10.1116/1.3106625]

I. INTRODUCTION

As device dimensions continue to decrease on integrated circuits, transition from Al-based interconnect to Cu-based interconnect is required for multilevel metallization to minimize the RC time delay. Cu-based interconnect shows greater resistance toward electromigration and lower resistivity, as compared to Al-based interconnect.1,2 As a result of the high diffusivity of Cu in Si and SiO$_2$ ($D_{Cu} \sim 2 \times 10^{-5}$ cm$^2$/s at 500 °C), high priority has been placed on developing Cu diffusion barriers.3 The presence of Cu in Si and SiO$_2$ causes serious degradation of the device performance associated with contact resistance, barrier height, $p$-$n$ junctions, contact layers, and electrical connections.4 Hence, an effective Cu diffusion barrier is required to block Cu transport and intermixing with adjacent dielectric materials for Cu interconnect technology.

Binary phase refractory metal nitrides such as tungsten nitride (WN$_x$) are promising candidates for replacing current diffusion barriers.5,6 WN$_x$ films show good thermal stability with Cu, acceptably low resistivities when deposited by CVD, and reasonable chemical mechanical planarization processing.7 The ternary phase material, tungsten carbonitrde (WN$_x$C$_y$), is also a promising candidate for diffusion barrier applications. WN$_x$C$_y$ film has low electrical resistivity, good adhesion to Cu, good resistance to Cu diffusion, and acceptable film growth on SiO$_2$. The efficacy of WN$_x$C$_y$ as a diffusion barrier has been demonstrated for films grown by both chemical vapor deposition (CVD)8,9 and atomic layer deposition (ALD).10,11 It has been shown that amorphous refractory ternary phase materials such as TiSi$_2$N$_y$, TaSi$_3$N$_y$, WSi$_2$N$_y$, and WB$_2$N$_y$ have better performance as Cu diffusion barriers than binary phase metal nitrides due to higher recrystallization temperature and thus lack of grain boundaries, which can serve as Cu diffusion pathways.12-15 Aerosol-assisted CVD (AACVD) is a useful technique for growing films of refractory metal nitrides because this technique has less stringent volatility restrictions in selecting precursors.16 Recently, we reported the synthesis of the diorganohydrazido(2-) tungsten complexes Cl$_4$(CH$_3$CN)W(NNR$_2$)$_2$ (1-3, R$_2$ = –(CH$_2$)$_5$–, Ph$_2$, Me$_2$) and Cl$_4$(pyridine)W(NNR$_2$)$_2$ (4, R$_2$ = Ph$_2$) by reacting 1,1-diorganohydrazines with tungsten hexachloride (WCl$_6$), followed by treatment with acetonitrile (CH$_3$CN) or pyridine (C$_5$H$_5$N).17 The tungsten piperidylhydrazido complex Cl$_4$(CH$_3$CN)W(N-pip) (1, R$_2$ = –(CH$_2$)$_5$–) was demonstrated to be a single-source precursor for the metal-organic CVD of WN$_x$C$_y$ thin films in the absence of NH$_3$. We now report the effect of NH$_3$ in the carrier gas on the properties of WN$_x$C$_y$.
thin films deposited from 1.

II. EXPERIMENTAL PROCEDURES

A. Precursor synthesis

Precursor 1 was prepared as described in the literature.\(^{17}\)

B. Film growth

The solid precursor 1 was dissolved in benzonitrile (PhCN) in a concentration of 8.1 mg/ml and then pumped into a nebulizer from a gas-tight syringe. A quartz plate in the nebulizer vibrates at a frequency of 1.44 MHz generating a mist of precursor and solvent, which is transported to the reactor in a carrier gas. Films were deposited using a vertical, quartz cold-wall CVD reactor on \(p\)-type boron-doped Si(100) single crystal substrates with electrical resistivity in the range of 1–2 \(\Omega\) cm. A radio-frequency (rf) heated graphite susceptor maintained the substrate at a constant temperature over a range of 300–700 °C. The reactor pressure was maintained at 350 Torr. The \(\mathrm{H}_2\) coreactant flow rate was 30 sccm, and the deposition time was 150 min.

C. Characterization

X-ray photoelectron spectroscopy (XPS) using a Perkin-Elmer PHI 5600 ESCA system was used to identify the chemical composition and the chemical bonding states of the elements in the film. A Philips APD 3720 x-ray diffraction (XRD) system was used to characterize the film microstructure. The surface roughness was measured using atomic force microscopy (AFM) with a Digital Instruments Dimension 3100 system. Cross-sectional scanning electron microscopy (SEM) on a JEOL JSM-6335F was used to measure the thickness of the film. The sheet resistance of the film was measured by four-point probe (Alessi Industries).

D. Diffusion barrier testing

\(\mathrm{Cu}\) was sputtered onto \(\text{WN}_x\text{C}_y/\text{Si}\) stacks to evaluate the performance of the diffusion barrier for application in \(\text{Cu}\) metallization. To prepare stacks for the test, \(\text{WN}_x\text{C}_y\) films (20 nm thick) were deposited by CVD at 400 °C on Si(100) single crystal substrates and then transferred via a load lock to the \(\text{Cu}\) deposition chamber with a base pressure of 3 \(\times 10^{-7}\) Torr. \(\text{Cu}\) (100 nm thick) was deposited by reactive sputtering using a Kurt Lesker CMS-18 multitarget sputter deposition system at room temperature and chamber pressure of 5 mTorr. The forward sputtering power for \(\text{Cu}\) was 200 W, while the \(\text{WN}_x\text{C}_y/\text{Si}\) stacks were rotated at 20 rpm during deposition. The \(\text{Cu}/\text{WN}_x\text{C}_y/\text{Si}\) stacks were then annealed in the CVD reactor at 500 °C for 30 min. Annealing was performed under \(\mathrm{N}_2\) to protect the \(\text{Cu}\) layer from oxidation. After annealing, the samples were analyzed by XRD and cross-sectional transmission electron microscopy (TEM). High resolution cross-sectional TEM images were taken using a JEOL TEM 2010F. TEM samples were prepared using a focused ion beam (FIB) equipped with a FEI Strata DB 235.

III. RESULTS AND DISCUSSION

A. Film structure

Figure 1(a) shows the progression of XRD patterns with increasing deposition temperature for films deposited in \(\text{NH}_3/\text{H}_2\) atmosphere. The XRD patterns shown in this figure have been compressed to include the results from all nine growth runs, and thus the resolution is diminished in the figure. An analysis of the original data, however, reveals four reflections, which were calibrated to the Si(400) diffraction peak. The reflections at 62.02 and 75.48 2\(\theta\) show low intensity, as compared to the primary ones at 37.48 and 42.78 2\(\theta\). The peak positions in these patterns are well matched with the same crystal structure. Both standards exhibited a face-centered-cubic structure with similar lattice parameter (\(\beta\)-\(\text{WN}_2\): 4.124 Å; \(\beta\)-\(\text{WC}_{1-x}\): 4.236 Å). In addition to the \(\text{WC}_{1-x}\) peaks, three sharp single crystal peaks were detected at 33.08, 61.76, and 69.14 2\(\theta\), and are associated with \(\text{Si}(200)\ K\alpha\), \(\text{Si}(400)\ K\beta\), and \(\text{Si}(400)\ K\alpha\) radiation, respectively.

The XRD spectra indicate that amorphous films were deposited from 300 to 450 °C, while polycrystalline materials
were deposited at and above 500 °C. The relative intensities of the four characteristic reflections are consistent with random grain orientation, and as expected, their variation with growth temperature follow the same pattern as the film thickness (Fig. 5). Note that Fig. 5 shows the growth rate data, which is proportional to film thickness since the growth time is constant for all runs. Primary peaks at 37.48 and 42.78 2θ are assigned to the (111) and (200) orientations, while the other two reflections at 62.02 and 75.48 2θ are attributed to (220) and (311) orientations, respectively. As the deposition temperature was increased from 500 to 600 °C, the peak intensities increased primarily as a result of increased film thickness and possibly changes in crystallinity. The intensities then successively decreased for the 650 and 700 °C deposited samples. This result is in contrast to that of the previous work using only H2 as the carrier gas in which the growth rate continued to increase with temperature (Fig. 5). The decreased intensity when NH3 is present is likely a result of precursor depletion from parasitic gas phase reactions. Transamination with NH3 has been postulated to remove the hydrocarbon group in the precursor, changing the rate-determining step, and thus the growth rate of the films deposited in the presence of NH3 is less than that for H2 only.

B. Surface morphology

The root-mean-square (rms) roughness of the surface of films deposited at 300 °C in the absence of NH3 was determined by AFM to be 0.99 nm, with a rise to 17.17 nm for deposition at 600 °C [Figs. 2(a) and 2(b)]. From the AFM micrographs in Figs. 2(c) and 2(d), the rms roughness of the film surface for films deposited in the presence of NH3 was 0.81 nm at 300 °C and 1.28 nm at 600 °C, indicating addition of NH3 results in films with smoother surfaces. The increase in surface roughness with the increase in the deposition temperature up to 600 °C is accompanied by increased crystallinity and grain size (Fig. 1). The decrease in roughness is consistent with an amorphous microstructure and more facile migration of absorbed species on the surface at higher deposition temperatures.

C. Chemical composition

Despite the presence of Cl in the precursor, no peaks were observed for either Cl 2p3/2 or Cl 2s at 199 and 270 eV, respectively, ruling out Cl contamination in the films within the detection limit of XPS (~1 at. %). The absence of Cl signals is consistent with prior computational results on the related imido complex ClH(CH3CN)W(NiPr), for which a mechanistic pathway was found for the reaction of the H2 carrier gas with W–Cl bonds to produce HCl in the gas phase. Figure 3(a) shows that the W levels have their highest value between 450 and 500 °C. Between 650 and 700 °C, the measured W levels in the films deposited with NH3 are higher than those in films deposited without NH3. This difference is related to the chemical bonding states of C 1s in Fig. 4. Between 650 and 700 °C, the Cl 1s binding energy (BE) shifted from lower BE to higher BE, indicating that amorphous C is more dominant than WCr. The increased extent of amorphous C formation dilutes the amount of W deposited. Figure 3(b) shows that the N levels increased over the entire temperature range after the addition of NH3. The highest N level for films deposited with NH3 (24 at. % at 400 °C) is greater than that of films without NH3 (18 at. % at 400 °C). NH3 coreactant is used as an additional N source, which allows deposition of high N level films compared to depositions without NH3. However, the increase in the flow rate of NH3 shows no significant variation in N levels. As deposition temperature increases up to 700 °C, the N levels drop gradually. For films deposited at 700 °C, the N levels in single-source deposition indicate an N concentration without including NH3 is 5 at. %, while for films deposited with NH3, the N increased to 12 at. %. For refractory metal nitride diffusion barriers, the N levels generally decrease with increasing deposition temperature in film deposited without NH3 and with NH3. It has been suggested that the higher deposition temperature increases the rate of N desorption as N2 gas, as evidenced in Fig. 3(b).

The results shown in Fig. 3(c) point to lower C levels in films deposited with NH3 than that in single-source deposition from 500 to 700 °C. The decrease in the C levels is attributed to increased competition from N when NH3 is present. Addition of NH3 seems to have no significant effect on the O levels in the films deposited below 500 °C, likely due to the lower reactivity at lower temperature. Figure 3(d) shows that deposition with NH3 has lower O levels than deposition without NH3. As the deposition temperature increased from 450 to 700 °C, the O levels in the presence and absence of NH3 decreased gradually to 5 at. %. The low O incorporation is consistent with dense WNxCy films at higher deposition temperature. Crystallization occurs to a greater extent at higher temperature reducing diffusion of O from air into the films.
D. Chemical bonding states

The values of the BE relative to the emitted kinetic energy (KE) determined by XPS were used to identify the elemental chemical bonding states. Figure 4 displays the evolution of XPS patterns for the W 4f BE as the deposition temperature is varied for films deposited with NH3. For films deposited at 300 °C, the W 4f BE is higher than WCx and WNx phases. The major W 4f7/2 and W 4f5/2 peaks for films deposited at 300 °C are at 36.8 and 37.7 eV, which are close to WO3 phase. These values for W 4f7/2 and W 4f5/2 peaks agree well with the reported values of 35.5–36.7 and 37.6–37.8 eV for the WO3 phase.24–27 As deposition temperature increases from 300 to 350 °C, the W 4f BE shifted from the higher BE for WO3 to the lower BE for WCx and WNx phases. The major W 4f7/2 and W 4f5/2 peaks for films deposited at 350 °C are at 31.7 and 33.7 eV, which are close to the reported values for WCx and WNx phases.25,26 From 350 to 700 °C, the major W 4f7/2 and W 4f5/2 peaks correspond to WCx and WNx phases, indicating that a chemical bonding state in W changes from a dominant WO3 phase to the mixture of β-WN2 and β-WC1−x phases or β-WNxC single solid solution as deposition temperature increases to 700 °C.

The evolution of XPS patterns for the N 1s BE with deposition temperature for films deposited with NH3 is summarized in Fig. 4b. The N 1s peak located at 397.3 eV is close to the reported value for WNx phase. This value agrees well with the reported values of 396.2–398.2 eV in WNx phase.24–26 It appears that the N in the film is bound to W in the WNx phase. The intensity of this N 1s peak is much higher over the entire temperature range, as compared to those for films deposited without NH3. Films deposited at 400 °C have the highest intensity of N, indicating the highest N levels in the films, as shown in Fig. 3(b). A single N 1s peak indicates that N has the same metal nitride bonding state over the entire temperature range, irrespective of the other components in the film. From 300 to 700 °C, there is only a single N 1s peak near 397.3 eV (i.e., no second N 1s peak near 400.0 eV).
XPS patterns for C 1s BE are shown in Fig. 4(c) over the range of deposition temperature for films deposited with NH$_3$. As shown in this figure, the BE of C 1s peak located at around 283.2 eV and corresponding to WC$_x$ phase is evident in films grown up to 650 °C. For films deposited at 700 °C, the bonding states of C 1s shifted from lower BE to higher BE. Deconvolution of the broad C 1s peak for films deposited at 700 °C using a Gaussian–Lorentzian function with background subtraction yields two separate peaks. The BE of C 1s peak located at 284.7 eV corresponds to amorphous C present outside of the $\beta$-WN$_x$C$_y$ nanocrystalline regions, while the BE of C 1s peak located at 283.4 eV corresponds to WC$_x$ in the $\beta$-WN$_x$C$_y$ nanocrystals. The former value for C 1s peak agrees well with the reported values of 284.2–285.2 eV for the amorphous C phase, while the latter value for C 1s peak agrees well with the reported values of 279.7–283.8 eV for the WC$_x$ phase.$^{25,26,29–32}$ Amorphous C begins to appear with the WC$_x$ phase in the film deposited at 700 °C in the presence of NH$_3$, while amorphous C appears at 650 °C in the absence of NH$_3$. This indicates that the addition of NH$_3$ promotes metal carbide bonding at higher temperature (650 °C).

O levels were also probed by XPS. Figure 4(d) traces the evolution of the O 1s BE with deposition temperature for films deposited with NH$_3$. The XPS pattern in O 1s BE over the entire temperature range is similar to that measured in films deposited with no added NH$_3$. The O 1s peaks were near 530.4 eV, which is close to the reported value for WO$_3$ phase. This value for the O 1s peak agrees well with the reported values of 528.2–531.6 eV for the WO$_3$ phase.$^{24–27}$

Fig. 4. Change in binding energies in (a) W 4f, (b) N 1s, (c) C 1s, and (d) O 1s with deposition temperature in the presence of NH$_3$. Data are from XPS after 10 min Ar$^+$ ion sputter.
As deposition temperature increases to 700 °C, the peak intensity of O 1s decreased as a result of film crystallization and C incorporation, blocking uptake along grain boundary.

E. Film growth rate

The growth rate in the presence of NH3 was low, in the range of 0.6–4.2 Å/min, as compared to the range of 2.7–29.4 Å/min for films deposited in the absence of NH3. Figure 5 shows the variation in growth rate with deposition temperature for films deposited with and without NH3. Both plots reveal a transition from a kinetically controlled growth regime to a mass transfer controlled one. Films deposited with NH3 had a transition point near 450 °C, while films deposited without NH3 had a slightly higher transition temperature near 500 °C. These differences in activation energy, transition temperature, and absolute growth rate are consistent with a change in the deposition mechanism due to the addition of NH3. It is also noted that the growth rate for films deposited with NH3 was decreased at higher temperature (650–700 °C), likely a result of precursor depletion in the gas phase near the substrate surface. Transamination with NH3 has been postulated to remove the hydrocarbon group in \(\text{I} \), changing the rate-determining step, and thus the growth rate of the films deposited with NH3 is different from that without added NH3.18

F. Electrical resistivity

The film resistivity was determined from measurement of the sheet resistance (four-point probe) and film thickness (cross-sectional SEM). The effect of growth temperature on the film resistivity for films deposited with NH3 is shown in Fig. 6. Films deposited at 300 °C show the lowest film resistivity (290 μΩ cm) and the values of film resistivity increase with the interplay of grain boundary density, film microstructure, film density, chemical bonding states, and film thickness over the entire temperature range. At lower deposition temperature, an increase in N levels bonded to W results in a decrease in film resistivity and at higher deposition temperature, an increase in film thickness results in an increase in film resistivity. Films deposited at 600 °C show the highest film resistivity (5450 μΩ cm). The resistivity for films deposited with NH3 at lower deposition temperature (350–450 °C) was lower than those deposited without NH3. This is attributed to increase in the film N content since the resistivity of WN is lower than WO3. At higher deposition temperature (500–700 °C), the film resistivity when deposited with NH3 was higher due to the decrease in C content since the resistivity of WN (4000 μΩ cm) is higher than that of WC (300–400 μΩ cm).33 The formation of WC is an important factor in decreasing film resistivity. This observation was confirmed by the XPS results for the bonding states of C in the films, as shown in Fig. 4. Hence, the proper combination of WN and WC is important in the formation of ternary-based refractory metal nitrides for diffusion barrier applications.

G. Diffusion barrier testing

XRD measurements were used to identify the formation of Cu3Si that occurs after barrier failure for Si substrates. As shown in Fig. 7, the XRD patterns show no reflections attrib-
Fig. 8. TEM cross-sectional images of Cu/WN$_3$C$_y$/Si stacks: [(a) and (b)] before annealing and [(c) and (d)] after annealing at 500 °C.

IV. CONCLUSIONS

The tungsten piperidylhydrazido complex Cl$_4$(CH$_3$CN)WN(pip) (I) was used to deposit WN$_3$C$_y$ with NH$_3$ as a co-reactant to investigate the effect of this co-reactant on the film properties for diffusion barrier applications. The deposited films show higher N levels with lower C incorporation as compared to films deposited without NH$_3$. XRD results suggest that films deposited at a lower deposition temperature (below 500 °C) were amorphous with crystallinity evolving at higher deposition temperature. The XPS W 4f phase indicates that most of the W is present as a mixture of WN$_x$ and WC$_x$ phases or a WN$_x$C$_y$ single solid solution. XPS results for both W and O indicate WO$_3$ is present at low deposition temperature (300 °C) in the amorphous state (XRD results) and as deposition temperature increases, WN$_3$C$_y$ becomes the dominant W phase rather than WO$_3$. XPS spectra of the O 1s bonding state show low O incorporation at higher temperature, which produces films with higher density. An examination of the XPS N 1s bonding state indicates that N is present in the WN$_x$ phase. XPS spectra show that films deposited at 400 °C have the highest N levels. The XPS C 1s bonding state results suggest that C is present as WC$_y$ and amorphous C. The C 1s BE is shifted from lower energy (283.1 eV) to higher energy (284.5 eV) for films deposited at 700 °C, indicating that amorphous C coexists with WC$_y$. The film growth rate with NH$_3$ addition varied in the range 0.6–4.2 Å/min over the entire temperature range of study. Strong film resistivity changes were observed and can result from various reasons including grain boundary density, film microstructure, chemical bonding states, and film thickness. Films deposited at 300 °C show the lowest film resistivity (290 μΩ cm), while the film resistivity was lower at low deposition temperatures as compared to films deposited without NH$_3$. WN$_3$C$_y$ thin films of 20 nm thickness were tested for barrier performance. The results show that WN$_3$C$_y$ films are viable diffusion barriers to prevent Cu interdiffusion and intermixing with Si after annealing under N$_2$ at 500 °C for 30 min.

ACKNOWLEDGMENTS

The authors would like to thank the National Science Foundation for support under NSF-CRC Grant No. CHE-0304810. They would also like to thank the Major Analytical Instrumentation Center (MAIC) at the University of Florida for assistance with XPS, XRD, SEM, AFM, FIB, and TEM, respectively.

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